Large magnetic entropy change and refrigerant capacity in rare-earth intermetallic RCuAl (R=Ho and Er) compounds

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ABSTRACT

The magnetic properties and the magnetocaloric effects of RCuAl (R=Ho and Er) compounds have been investigated. Both HoCuAl and ErCuAl just undergo a second-order ferromagnetic–paramagnetic phase transition at T_C. Large reversible magnetic entropy changes (ΔS_M) are observed around their respective Curie temperatures due to the ferromagnetic–paramagnetic phase transition. For a field change of 0–5 T, the peak values of $-\Delta S_M$ of RCuAl (R=Ho and Er) compounds are 23.9 and 22.9 J kg^{-1} K^{-1} at T_C, with the values of refrigerant capacity of 393 and 321 J kg^{-1}, respectively. These properties suggest that RCuAl (R=Ho and Er) compounds could be considered as attractive magnetic refrigerants working in low temperature range.

Recently, much attention has been paid to magnetic refrigeration based on the magnetocaloric effect (MCE) of solid-state working substances [1–4]. Magnetocaloric materials with a first-order phase transition have been widely investigated due to their large isothermal magnetic entropy change (ΔS_M), an important parameter for evaluating the magnitude of MCE. However, some problems such as hysteresis and time dependence, which exist almost universally in magnetocaloric materials with a first-order phase transition, should be solved before this kind of materials is practically used. Magnetocaloric materials with a second-order phase transition may have a lower peak value of ΔS_M, whereas this could be compensated by their large refrigerant capacity (RC), which is a more crucial parameter for evaluating the technological significance in a refrigerant material. Therefore, it is necessary to explore new magnetocaloric materials with a second-order phase transition.

RCuAl (R=heavy rare-earth) compounds each crystallizing in a hexagonal ZrNiAl-type structure belong to a large family of terminal RTX (T=transitional metal, X=p-metal) intermetallics. All the R atoms and Al atoms occupy 3g and 3f sites, respectively. Cu atoms occupy two non-equivalent 1b and 2c positions [5]. Two types of basal plane layers are alternately distributed along the c-axis: one contains all the R atoms and one-third of Cu atoms, and the other comprises a nonmagnetic layer formed by all the

Al atoms and two-thirds of Cu atoms (see the inset of Fig. 1). The distinct layered character of the crystalline structure may lead to large magnetocrystalline anisotropy.

In the recent years, magnetic structures, phase transitions, and magnetic properties for RCuAl (R=Gd–Er) compounds have been investigated in detail by neutron diffraction, specific heat, and magnetic measurements [6–11]. Uniaxial magnetic anisotropies in GdCuAl, DyCuAl and ErCuAl and a basal-plane type of magnetic anisotropy in HoCuAl have been found. The magnetic structure is collinear whereas the spins are not parallel to the c-axis for TbCuAl. In previous work, we have reported the magnetic properties and magnetocaloric effects of RCuAl (R=Gd, Tb and Dy) compounds [12–14]. Large reversible magnetocaloric effects make them attractive candidates for magnetic refrigeration. In this paper, MCEs and refrigerant capacities of RCuAl (R=Ho and Er) compounds with diverse magnetic anisotropy are reported contrastively. Large ΔS_M and RC are obtained for RCuAl (R=Ho and Er) compounds around their respective Curie temperature. For a field change of 0–5 T, the maximum values of $-\Delta S_M$ are 23.9 and 22.9 J kg^{-1} K^{-1} for RCuAl (R=Ho and Er) compounds, respectively. The corresponding RC values reach 393 and 321 J kg^{-1} for the same field change.

The RCuAl (R=Ho and Er) ingots were prepared by arc melting Al, with a purity of 99.99 wt%, and R and Cu, with a purity of 99.9 wt%, in a high-purity argon atmosphere. 5 at% excessive Ho and 2 at% excessive Er were used to compensate the weight loss during the arc melting. The melt-spun ribbons were obtained by using a single-roller melt-spinner at a cooper wheel surface speed of 50 m/s. A post-annealing of the products at 873 K for 100 h and

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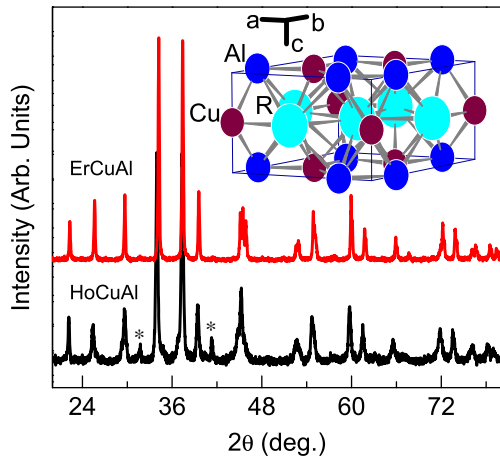E-mail address: happylaugh746@gmail.com (Q.Y. Dong).

Fig. 1. X-ray diffraction patterns of RCuAl (R=Ho and Er) compounds at room temperature. Inset: schematic drawing of the ZrNiAl-type unit cell of RCuAl.
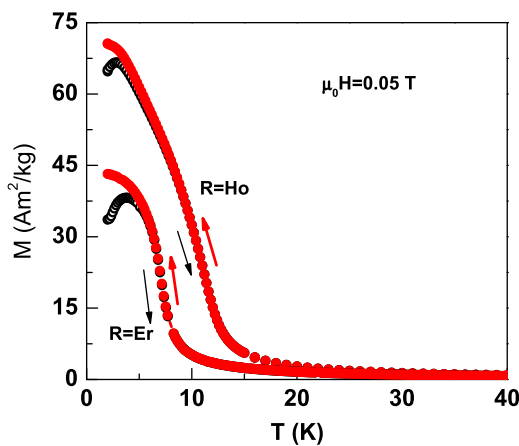

Fig. 2. ZFC (open symbol) and FC (closed symbol) temperature-dependent magnetizations under a magnetic field of 0.05 T for RCuAl (R=Ho and Er) compounds.

a subsequent quenching to room temperature were performed to obtain crystalline samples. The crystalline structures of samples are determined by a X-ray powder diffractometer. Magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer.

XRD patterns at room temperature (Fig. 1) indicate that RCuAl (R=Ho and Er) compounds crystallize in a hexagonal ZrNiAl-type structure except for the presence of a minor Al_2O_3 phase marked by "*" in the HoCuAl compound. The much higher volatility of Ho than Er during the arc melting leads to the excess of Cu and Al. The reaction between Al and the residual Oxygen in the furnace may result in the formation of Al_2O_3 phase. The nonexistence of Cu or the Cu-based alloys may be due to the large solution of Cu in the HoCuAl phase. However, this explanation needs to be verified experimentally in the future. By calculation, it is found that the lattice parameters reduce from a=6.977 Å and c=4.006 Å for the HoCuAl compound to a=6.970 Å and c=3.995 Å for the ErCuAl compound, according with the lanthanide contraction law of rare-earth intermetallic compounds. These values are almost consistent with the results of Ref. [7].

The zero-field-cooling (ZFC) and field-cooling (FC) temperature dependences of magnetizations for RCuAl (R=Ho and Er) compounds under a low magnetic field of 0.05 T are shown in Fig. 2. A magnetic phase transition takes place at Curie temperature (T_C), corresponding to the maximum slope of M–T curve.

The values of T_C for RCuAl (R=Ho and Er) compounds are 12 K and 7 K, respectively [7]. It can be seen from Fig. 2 that the ZFC and FC curves are completely reversible in the vicinity of T_C for these two samples, which is characteristic of a second-order transition. Meanwhile, a significant thermal irreversibility between the ZFC and FC branches and a maximum value of the magnetization on the ZFC branch are clearly observed at low temperatures for two compounds. It has been verified by neutron diffraction, specific heat and AC-susceptibility investigations that the ErCuAl compound undergoes only a magnetic phase transition: ferromagnetic–paramagnetic transition at T_C [6]. Moreover, all the Er atoms carry the same magnetic moments and are aligned ferromagnetically along the c-axis below T_C. The X-ray diffraction result in Ref. [8] indicates that HoCuAl also experiences only a ferromagnetic–paramagnetic phase transition and shows a basal-plane type magnetic anisotropy. The impure phase Al_2O_3 does not affect obviously the shape of thermal magnetization curves due to its diamagnetism. Therefore, the discrepancy between ZFC and FC M–T curves for RCuAl (R=Ho and Er) compounds may be attributed to the domain wall pinning effect.

The nature of magnetic phase transition and MCEs of RCuAl (R=Ho and Er) compounds are investigated via the measurements of isothermal magnetization curves at different temperatures. The Arrott plots [15] and the temperature dependences of ΔS_M for RCuAl (R=Ho and Er) compounds are displayed in Fig. 3. The positive slopes of Arrott plots near T_C (see the left panels of Fig. 3) confirm the second-order FM–PM transition, which accords well with the case mentioned based on Fig. 2 where thermal hysteresis around T_C is absent. From the right panels of Fig. 3, one can find that both HoCuAl and ErCuAl compounds exhibit large ΔS_M around their respective Curie temperatures. For a magnetic field change of 0–2 T, the peak values of $-\Delta S_M$ for RCuAl (R=Ho and Er) compounds are 14.0 and 14.7 J kg^{-1} K^{-1}, respectively. The corresponding maximum values of $-\Delta S_M$ increase to 23.9 and 22.9 J kg^{-1} K^{-1} for a magnetic field change of 0–5 T. In magnetocaloric materials RTAl (R=rare earth, T=Co and Ni) ever reported with a second-order phase transition, the peak value of $-\Delta S_M$ for HoCoAl compound with the $MgZn_2$-type structure is 21.5 J kg^{-1} K^{-1} at T_C=10 K for a field change of 0–5 T [16]. The maximum values of ΔS_M are 23.6 J kg^{-1} K^{-1} at T_C=14 K for HoNiAl and 21.6 J kg^{-1} K^{-1} around T_N=5.6 K for ErNiAl with the ZrNiAl-type structure for the same field change [17,18]. The peak values of $-\Delta S_M$ for the present samples can also be comparable to or even larger than those of some other magnetocaloric materials with a similar phase transition temperature for the same field change, such as $DyNi_5$ (15.4 J kg^{-1} K^{-1} at T_C=12 K) [19], DySb (15.8 J kg^{-1} K^{-1} at T_N=11 K) [20], HoCuSi (33.1 J kg^{-1} K^{-1} around T_N=9 K) [21] and so on.

Besides the peak value of ΔS_M, RC is another important parameter for characterizing the MCE. In the present paper, the value of RC is calculated by numerically integrating the area under the ΔS_M–T curve, with the temperatures at half maximum of the peak taken as the integration limits [22]. Large RC values of 393 J kg^{-1} and 321 J kg^{-1} are obtained in RCuAl compounds with R=Ho and Er for a magnetic field change of 0–5 T, respectively. The RC of HoCuSi is also calculated from the $-\Delta S_M$ versus T curve in Ref. [21] by the same method. The evaluated value of RC for HoCuSi is 385 J kg^{-1} for the same field change, which is slightly less than that of HoCuAl, although the ΔS_M value of the former is much larger than that of the latter. Moreover, the RC of HoCuAl is also comparable to that of $ErAl_2$ (RC=397 J kg^{-1} for a field change of 0–5 T), though the ΔS_M value for $ErAl_2$ reaches 40 J kg^{-1} K^{-1} at T_C=13 K [23].

In conclusion, the RCuAl (R=Ho and Er) compounds with the hexagonal ZrNiAl-type structure show large reversible ΔS_M around their respective Curie temperatures. For a magnetic field
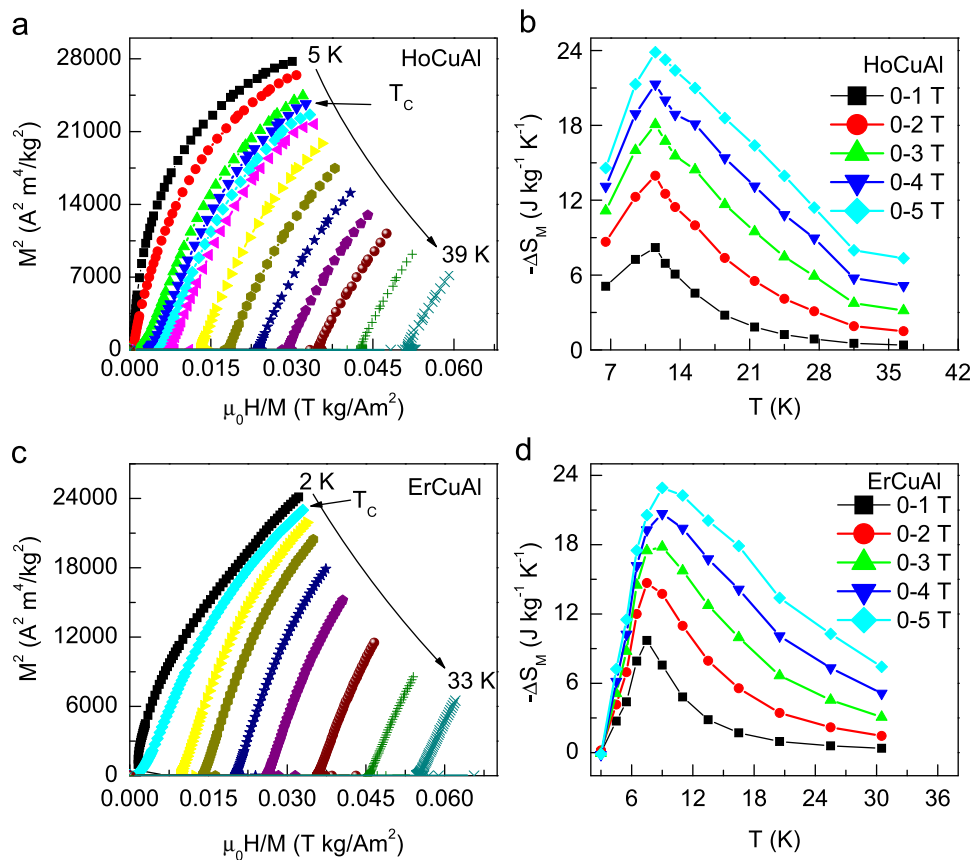
Fig. 3. Arrott plots ((a) and (b)) and isothermal magnetic entropy changes as functions of temperature under typical field changes ((c) and (d)) for RCuAl (R=Ho and Er) compounds, respectively.

change of 0–5 T, the maximum values of $-\Delta S_M$ for RCuAl (R=Ho and Er) compounds are 23.9 and 22.9 J kg^{-1} K^{-1}, respectively. Corresponding large RC values are also obtained, which are 393 and 321 J kg^{-1} for the same field change. The large ΔS_M and the high RC as well as no hysteresis loss make RCuAl (R=Ho and Er) compounds promising candidates for magnetic refrigeration near liquid-helium temperatures.

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